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Adduct formed by chromium trioxide and zwitterionic quinolinic acid

Invited Paper

Markku R. Sundberg*[a], Rolf Å. M. Uggla[a], Reijo J. Sillanpää[b], Krzysztof K. Zborowski[c], Angel Sánchez-González[d], Jorma K.T. Matikainen[e], Seppo A. A. Kaltia[e] and Tapio A. Hase[e]

[a]*Department of Chemistry, Laboratory of Inorganic Chemistry, PO Box 55, University of Helsinki, FIN-00014 Helsinki, Finland*

[b]*Department of Chemistry, Laboratory of Inorganic Chemistry, University of Jyväskylä, PO Box 35, FIN-40351 Jyväskylä, Finland*

[c]*Faculty of Chemistry, Jagiellonian University, 30-060 Kraków, Poland*

[d]*Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy*

[e]*Department of Chemistry, Laboratory of Organic Chemistry, PO Box 55, University of Helsinki, FIN-00014 Helsinki, Finland*

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Abstract: Chromium trioxide forms an adduct with zwitterionic quinolinic acid. The structure of the product was found to be (quinolinium-3-carboxylato-*O*)trioxidochromium(VI), determined by single-crystal X-ray diffraction methods. To evaluate the bonding properties of the compound, its structure was optimized at the B3LYP/6-311G* level of theory. The electronic characteristics were investigated by topological methods applied to the total charge density in various model compounds including the title compound, title compound with a HF molecule presenting a hydrogen bonding and anionic moiety. Calculated aromaticity indices indicate that the quinolinic rings tend to conserve their degree of aromaticity against hydrogen bonding. However, when there is hydrogen bonding involving an N-H bond or when the quinolinium zwitterion is deprotonated, there are clear changes in the interaction between chromium trioxide and the quinolinic moiety.

Keywords: *chromium trioxide complexes electronic properties •aromaticity •AIM •ELF*

1. Introduction

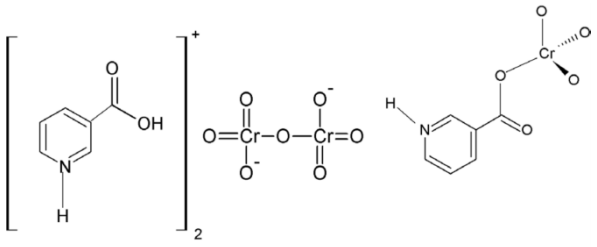
Oxidation of organic molecules by oxochromium(VI) species has been a well-known tool in organic chemistry [1]. The chromate anion is known to form in acidic aqueous solutions, both chromatosulfate [2] and chromatophosphate [3] anions have precedent. Later on, two diesters formed by chromic and cedric acid, as Patchouli alcohols were reported, where chromium has retained its oxidation state +6 were also reported [4]. In a reaction between chromium trioxide (CrO_3) with Ph_3CCl another diester is produced [5].

Quite surprisingly, chromic acid seems to form products not only with alcohols, but also with acids. A new variant in the pyridine-Cr(VI) family of oxidizing agents was introduced by Lopez et al. [6]. The authors in [6] claimed that the structure would be a salt of nicotinic acid and dichromate anion 1. This assumption was also made later on in a review concerning chromium(VI) oxidants [7]. On the other hand, a wide range of the so-called substituted chromate ions have been shown to have a donor-acceptor interaction between a ligand and CrO_3 [8]. Furthermore, we showed by using single-crystal X-ray methods that the structure of compound 1, in the solid state, actually contains a zwitterion coordinated to chromium trioxide 2 (Scheme 1) [9].

Zwitterionic species are employed as valuable reagents in organic synthesis since they offer some special features of reactivity [10]. It is interesting to note that pyridine forms a stable crystalline 2:1 Lewis acid - base complex with chromium trioxide. When benzimidazole and three 2-alky-1H-imidazoles were treated with chromium trioxide in aqueous acetic acid, dichromate salts were obtained [11].

Zwitterionic chromium(VI) compounds have been used to oxidize alcohols to carbonyl compounds. We

* *E-mail: markku.sundberg@helsinki.fi*



1 2

Scheme 1. Structures of the nicotinic acid – dichromate anion salt and the nicotinic acid chromium trioxide complex.

have utilized compound 2 in the synthesis of haminols [12], pulo'upone [13] and isopulo'upone [14]. The reaction mechanisms remain uncertain. It seems that the reactions might be base-catalyzed, as reported in [6]. Computational study is available only for chromyl chloride as an oxidation agent [15].

To gain more insight into electronic properties of the zwitterionic chromium(VI) compounds, we synthesized a new adduct of chromium trioxide with quinolinic acid. We report here the structure of quinolium-3-carboxylato-O)trioxidochromium(VI) (referred as **3** hereafter) characterized by single crystal X-ray methods. Moreover, we carried out its structure optimization using DFT methods to get better insight into the electronic properties of the zwitterionic adduct. Topological methods were applied to analyze charge density in the optimized complex. Influence of hydrogen bonding on the aromaticity in the complex was also investigated.

2. Experimental Procedure

2.1. Synthesis

Chromium trioxide (1.2 g, 12.0 mmol) and 3-quinolinic acid (1.0 g, 5.8 mmol) were mixed in water (3.0 mL). After the reaction mixture turned yellow forming a solid precipitate, the solid phase was separated by suction filtration and washed with acetone (30 mL) and dichloromethane (10 mL) and air-dried to give 1.2 g (yield, 75 %) of crude product. 100 mg of this product were dissolved in 20 mL of warm water and left at room temperature for a few hours. After a precipitate was formed, a portion of the brown-yellow clear solution above it was transferred to an Erlenmeyer flask, closed partially so that water could only slowly evaporate. After standing at ambient temperature for one month, small crystals were formed that were used for X-ray diffraction study and for elemental analyses. Anal. Calc. for $C_{10}H_7CrNO_5$: C, 43.97; H, 2.58; N, 5.13. Found C, 42.6; H, 2.90; N, 5.03.

2.2. IR measurement.

The IR spectrum was run from a powder sample by using Perkin Elmer Spectrum One FT-IR/ATR spectrometer.

2.3. X-Ray structure determination.

Reflection data was collected by using a Rigaku AFC5S diffractometer with graphite monochromated Mo-K_α radiation, λ = 0.71072 Å, T = 293(2) K, ω-2θ scan mode and scan speed 8° min^{-1}. The data set was corrected for Lorentz and polarization effects. An empirical absorption correction based upon azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.73 to 0.80 [16]. The structure was solved by direct methods using the SHELXS-97 program [17] and full-matrix least-squares refinements on F2 were performed using the SHELXL-97 program [17]. The non-hydrogen atoms were refined with anisotropic displacement parameters and the NH hydrogen atom isotropically with the fixed displacement parameter (1.2 times larger than that of the N atom). The CH hydrogen atoms were included at the fixed distances with fixed displacement parameters from their host atoms (1.2 times larger than that of the N atom). The final R1-value was 0.042 [I > 2s(I)] based on F2. The figures were drawn with Ortep-3 for Windows [18]. Selected Crystal data and structure refinement for 3exp are reported in Table 1. The data have been deposited at the Cambridge Structural Database and the CCDC 720018 contains the supplementary crystallographic data for (quinolinium-3-carboxylato-O) trioxidochromium(VI). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK;

Table 1. Crystal data and structure refinement for (quinolinium-3-

Empirical formula	$C_{10}H_7CrNO_5$
Formula Weight	273.17
Crystal System	Monoclinic
Space group	P21/c (No. 14)
a /Å	9.7035(17)
b	12.183(3)
c	8.841(2)
β /°	98.039(17)
V /Å^3	1034.9(4)
Z	4
Dcalc /g cm^{-3}	1.753
μ(MoK_α) /mm^{-1}	1.114
Crystal Size /mm	0.20 x 0.22 x 0.38
T /K	294
$\theta_{Min-Max}$ /°	2.1, 27.5
Reflections measured	2668
Unique reflections	2347
Observed data [I > 2.0σ(I)]	1770
R	0.0415
wR^2	0.1181
S	1.09

fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional details for the X-ray determination are given as Supplementary Material.

2.4. Computational methods.

The structures were optimized by DFT methods at the B3LYP/6-311G* level of theory by applying Gaussian program suite [19] installed on the HP CP4000 BL ProLiant supercluster at CSC Helsinki. Experimentally measured geometries of studies compounds were used where possible. If not, appropriate starting structures were projected *in silico* and optimized. The charge density of the structures was then investigated by topological QTAIM methods [20]. A more detailed description of the parameters in bond critical point is given in our earlier paper [21] and in [20]. The programs used were MORPHY98 [22], AIM2000 [23], and AIMPAC [24]. Further, Electron Localization Function (ELF) method was employed by using the TopMod program [25]. Atomic charges were computed by integration of the electron density within atomic basins using MORPHY and AIMPAC. The values of integrated Laplacian were taken as the measure of the quality of integration. In theory Laplacian values should be equal to zero but it had been shown that values smaller than 1×10^{-3} provide only negligible errors in obtained molecular properties [26]. Figures were created by PLUTON [27], MORPHY and TopMod.

Aromaticity indices based on geometric (HOMA) and magnetic (NICS) criteria of aromaticity [28] were employed in this study. The HOMA index was calculated using the equation: $HOMA = 1 - [\alpha/N \sum (R_{opt} - R_i)^2]$ [29], where R_{opt} and R_i are optimal bond lengths and bond lengths in the real system, respectively. The empirical factor α sets the HOMA value equal to 0.0 for the Kekulé structure of benzene (treated as non-aromatic compound) and 1.0 for the real benzene structure (treated as fully aromatic compound). N is the number of bonds of the studied system. NICS (Nucleus Independent Chemical Shift) was originally defined as the negative value of the magnetic shielding computed at the aromatic ring center [30] (now this method is known as the NICS(0) index). Since then, other NICS techniques have been introduced. Among them, the NICS(1) method is the most popular one. In this index, magnetic shielding is calculated (in order to avoid strong influence of sigma electrons) 1 Å above the ring center of the system under consideration [31]. Highly negative NICS values denote aromaticity, whereas systems with positive values are antiaromatic. Magnetic properties of studied compounds were calculated under the GIAO [32] approximation using their B3LYP/6-311G(d,p) geometries.

3. Results and Discussion

3.1. Structure in the solid state.

The structure of the (quinolinium-3-carboxylato-*O*) trioxidochromium(VI) ($\mathbf{3}_{exp}$) is shown in Fig. 1 with the labeling scheme. Selected bond lenghts and angles are given in Table 2, which will also be discussed later on, with the computed values. More data are available as Supplementary Material. The molecular structure of the compound is similar to the structure of the nicotinium-3-carboxylato-*O*)trioxidochromium(VI) (compound **2**, Scheme 1) reported by us previously [9]. Both **2** and $\mathbf{3}_{exp}$ consist of monomeric units. Chromium trioxide probably forms a coordinate bond with the oxygen O4,

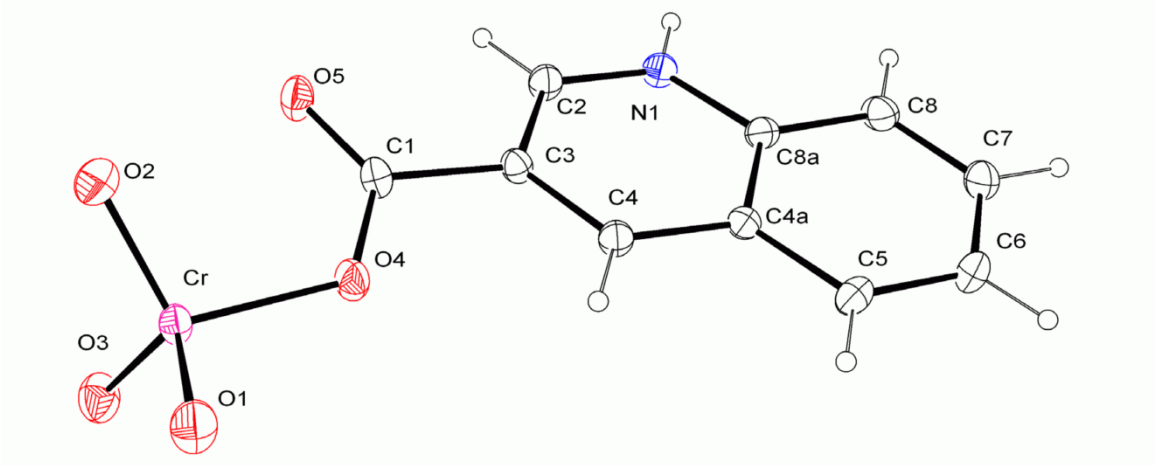


Figure 1. ORTEP view of (quinolinium-3-carboxylato-O)trioxidochromium(VI) showing the atom numbering. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% level of probability.

since the Cr-O1-O2-O3 moiety is not planar. The formal oxidation state of chromium is VI, and the structure is protonated at the nitrogen atom in the aromatic ring. The crystal structures consist of the zwitterions connected by hydrogen bonding networks.

The three Cr-O bond lengths in the alcoholic complex can be divided into two categories, corresponding to single [1.736(2) Å] and double [1.578(2) Å] bonds. In the present compounds, all three of the nonbonded oxygens have very similar distances to chromium, and they are slightly elongated having the range 1.600(3)-1.604(3) Å. The fourth Cr-O bond length of 1.874(2) Å is clearly longer in the present compound than in the complex with the alcohol [1.736(2) Å]. The value is slightly longer than the sum of ionic radii of 1.80 Å [33]. On the other hand, the bond length O4-C1 is 1.304(4) Å in the present compound, whereas in the alcoholic complex the respective value is 1.461(3) Å.

The most significant difference between the structures of **2** and **3** is that the present compound **3** does not adopt the strict crystallographic *m* symmetry as **2** does (with the exception of two of the oxygen atoms connected to chromium). The only highly significant difference in the bond lengths of the compounds is seen in the values of N-C. In the present compound **3** they are mutually different, 1.379(4) and 1.310(4) Å, whereas in **2** the respective values are 1.333(4) and 1.334(4) Å. Also the bond angles are generally very similar. The only difference is seen in the Cr-O-C angles, which are 118.3(2) and 123.7(2)° for **2** and $\mathbf{3}_{exp}$, respectively. The molecules in $\mathbf{3}_{exp}$ form chains connected by hydrogen bonds depicted in Fig. 2. The respective parameters are as follows: H1•••O5^{i} = 2.00, N1•••O5^{i} = 2.850(4) Å and N1-H1•••O5^{i} = 168.0° (i = 2-x, -0.5+y, 1.5-z).

To study further the packing, we recorded the IR spectra for the title compound. The carboxylate stretchings appear at 1651 and 1377 cm^{-1}, for the ν_s and ν_{as}, respectively. The difference of 274 cm^{-1} is in the range of 107-565 reported for the unidentate acetate groups [34]. The ν_s band for the carboxylate stretching for chromyl acetate appears at 1710 cm^{-1} [35].

The existence of hydrogen bonding in the experimental structure is also seen in the N-H stretching frequency. The value obtained for the optimized structure is 3510 cm^{-1}, whereas in the experimental IR spectrum it is found as a broad band in the range of 3100-1950 cm^{-1}. Red shifting and broadening are indicative of hydrogen bonding.

3.2. Computational studies.

There are two main questions that the single-crystal X-ray study cannot resolve. These are: i) what kind of influence a hydrogen bond could have on the electronic properties and ii) what kind of interaction there would be between chromium and the zwitterion. To study these questions, various computations were carried out. We performed the structure optimization for the title compound by using DFT methods at the B3LYP/6-311G* level of theory. Various other structures were optimized

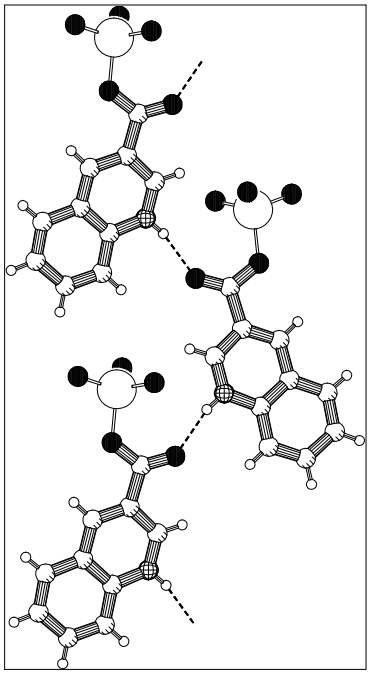


Figure 2. PLUTON view of the intermolecular hydrogen bonding system in the solid state of (quinolinium-3-carboxylato-O) trioxidochromium(VI).

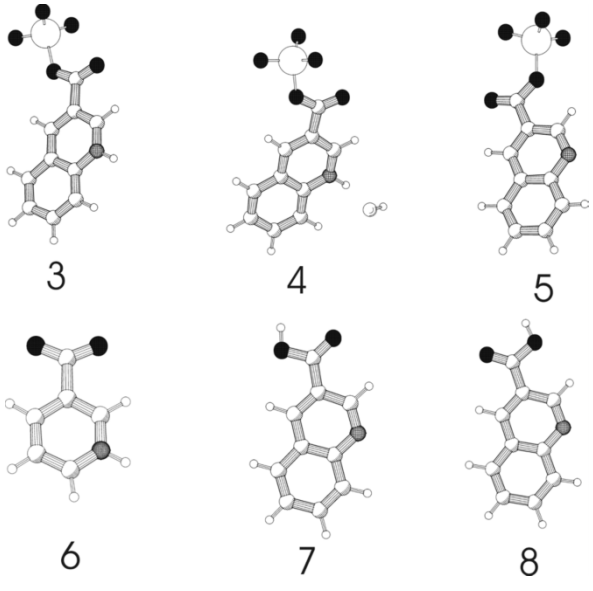


Figure 3. The optimized structures 3 - 8 at the b3lyp/6-311G* level of theory.

for comparison purposes, too. They are shown in Fig. 3.

Both point groups C_s and C_1 were considered for the structures. The difference in the optimized energies was minimal, less than 0.0001 kcal mol^{-1}. Such difference indicates that the deviation from the C_s symmetry found in the solid state of $\mathbf{3}_{exp}$ must be caused by intermolecular interactions. Indeed, as presented in Fig. 2, there exists an intermolecular hydrogen bonding network. As a model system we optimized the model complex of the studied compound with a HF molecule pointing to the hydrogen atom of the –N-H group. It is noteworthy, that in this case the structure with a symmetry plane does not present a true energy minimum. Only when the point group is C_1, are there no imaginary vibrational frequencies. The geometrical parameters for the optimized structures are given in Table 2 and compared with the experimental values. Furthermore, we also optimized the anionic moiety (compound **5**).

There are some differences between theoretical and experimental Cr-O bond lengths. The optimized values tend to be shorter for the terminal Cr-O bonds. The fourth Cr-O distance shows an opposite behaviour.

Table 2. Selected geometrical parameters for the experimental structure and for optimized structures 3 -5 at the B3LYP/6-311G* level.

	experimental	3	4	5
Cr-O1	1.601(3)	1.582	1.582	1.586
Cr-O2	1.600(3)	1.585	1.585	1.589
Cr-O3	1.604(3)	1.582	1.582	1.586
Cr-O4	1.874(2)	1.929	1.927	1.901
C1-O4	1.304(3)	1.283	1.284	1.304
C1-O5	1.219(4)	1.216	1.217	1.217
C1-C3	1.499(4)	1.527	1.526	1.516

A plausible explanation for this is the hydrogen bonding network in the solid state, which is not included for the optimization. In the anionic moiety the Cr-O bond lengths are slightly nearer to the experimental values. Another systematic difference is the orientation of the CrO_3. In the experimental structure the dihedral angle of -37.7(3)° for O2-Cr-O4-C1 indicates a clear non-planarity. In the optimized structures $\mathbf{3}_{opt}$ and **5** the dihedral angle is 0°. The Cr-O4 bond length shortens in the anionic moiety while the C1-O4 bond is elongated.

To estimate the effect of the hydrogen bonding on the quinolinic moiety, we calculated the Electron Localization Function (ELF) isosurfaces for structures **3** and **4** and they are shown in Fig. 4.

The isosurfaces in the two structures are almost identical in the quinolinic part, which implies that the effect of added hydrogen fluoride does not have a big influence on the electronic structure of studied compound. However, there is a marked effect on the hydrogen attached to nitrogen. The ELF study shows a special H basin for the proton bonded to N atom. This basin has a lower volume with respect to the other H basins, and the population of this basin has a normal value very close to 2 electrons. The low volume indicates repulsion between two different electron densities, *i.e.* the electron density of the hydrogenated basin, and the electron density of the valence shell belong to F. It is noteworthy that if we decreased the isovalue (the plot would increase) the two densities would avoid the contact. This means that there is a weak and electrostatic interaction between hydrogen of the –N-H group and fluorine.

The delocalization index, introduced by Fradera, Austen and Bader [36] is a useful tool that measures the amount of electrons shared between two atomic

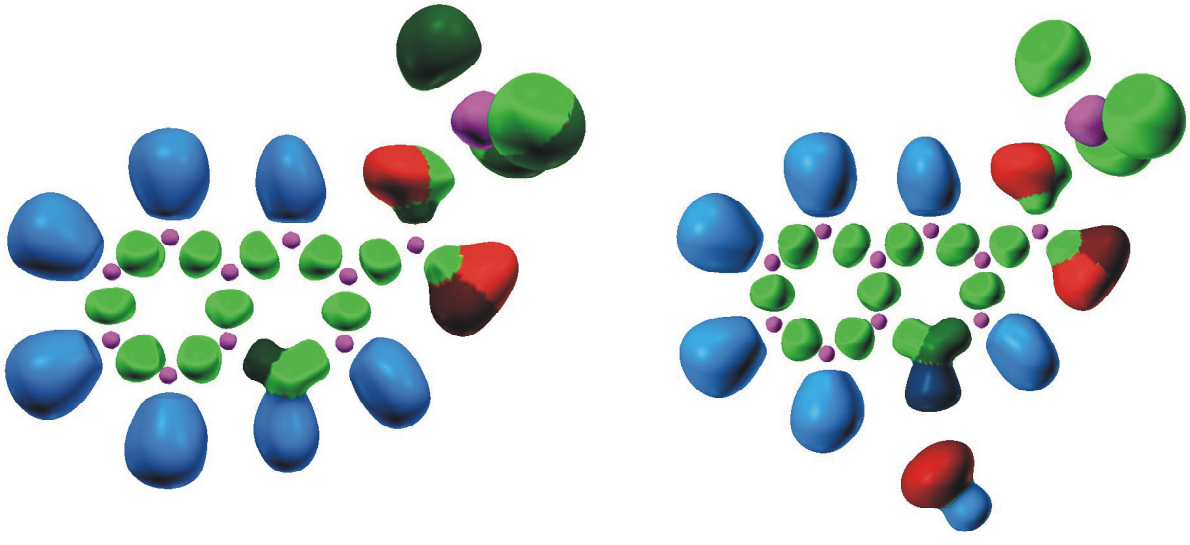


Figure 4. The ELF isosurfaces drawn at 0.70 for the structures without (3, left) and with (4, right) hydrogen fluoride.

basins, so is an indication of the bond order. This index for the F and the proton bonded to the N atom gives an extremely low value of 0.06, indicating a electrostatic weak interaction.

To get a more precise insigth into the aromaticity of the studied systems, we calculated values of some aromaticity indices. (Quinolinium-3-carboxylato-*O*) trioxidochromium(VI) consists of two fused rings, a benzene one and a pyridine one. Benzene is usually considered as the symbol of aromaticity. Also pyridine is commonly known as a compound with a strong π-electron delocalization. Reported in the literature (all presented NICS values for benzene, pyridine and quinoline are taken from the [37] and were calculated on the B3LYP/6-311+G** level of theory) NICS values for benzene are -8.03 (NICS(0)) and –10.20 (NICS(1)). Predicted by these indices aromaticity of the pyridine is a bit lower, (NICS(0) = -6.82 and NICS(1)=-10.17. NICS values for quinoline, are slightly more negative denoting stronger aromaticity (carbocyclic ring of quinoline: NICS(0) = -8.81, NICS(1) = -10.83; heterocyclic ring of quinoline: NICS(0) -7.50, NICS(1) = -10.52). Our calculated NICS values for **6** (see Table 3) show that the carboxylic moiety does not influence the electronic structure of quinoline. Observed discrepancies can be simply the result of the small difference in the basis set used in the cited paper and our calculations. On the other hand, HOMA index predicts small decreasing of electron delocalization from benzene and pyridine to the studied compound. Reference HOMA value for benzene is equal 1.00 and corresponding value for pyridine is 0.99 [38], both values calculated for experimental geometries. In general we can conclude that both aromaticity indices predict a high level of π-electron delocalization in the compound under investigation.

To study the influence of an additional aromatic ring, we optimized also the structure of quinolinic acid, Fig. 3. There are two possible conformers, where the labile proton is connected with the carboxylic group, namely **7** and **8**. Compound **6** represents the zwitterionic form. For both methods, HOMA and NICS, differences in the aromaticity levels predicted for described conformers **7** and **8** are negligible. It is known that heterocycles like pyridine and quinoline conserve their aromaticity during protonation [39]. So, not surprisingly, no dramatic changes in aromaticity between **6** and conformers **7** and **8** are observed. Usually slightly higher level of aromaticity is predicted for the zwitterionic **6**. The opposite tendency is noticed only for the NICS(1) in the pyridine ring.

Influence of metal ions on aromaticity of organic ligands is so far seldom investigated with different conclusions about its strength [40-43]. In our case, complexation of the CrO_3 moiety to the deprotonated carboxylic group does not affect the electron delocalization of the quinoline system (see Table 3). No change is observed in the HOMA method and negligible differences are noticed between NICS values. Introduction of the intermolecular hydrogen bond between the complex **3** and hydrogen fluoride also does not change the aromaticity level of the studied compound. Influence of the intermolecular hydrogen bond on the aromaticity is even less popular topic than mentioned above influence of metal ions. So far, a detailed study was performed for substituted phenols interacted with various bases [44,45]. For phenols, the influence of the intermolecular hydrogen bonds can be quite significant. Our results seem to suggest that such an effect in the case of the protonated pyridine ring is small.

The general conclusion about aromaticity of the studied compound is that quinoline system, as a strong aromatic system, is able to conserve its degree of aromaticity regardless of all disturbances presented above. It acts in similar way as benzene, where attaching various substituents influences very weakly the π-electron delocalization of the ring [46,47].

QTAIM methods were applied to analyze the interaction between chromium and the nearest oxygen of an adjacent quinolinic moiety. The results are given in Table 3. We may say that there is a chemical bond between Cr and O4 in each moiety, because a bond path was found between them with a bond critical point (bcp) (Fig. 5). The charge density in each bcp is rather low, as is also the case with the Laplacian values for the hydrogen bonded moiety and anion.

The effect of hydrogen bonding on the bonding

Table 3. Aromaticity data for carbocyclic and heterocyclic (in parentheses) rings of optimized compounds.

Compound	6	7	8	3	4
HOMA	0.86 (0.88)	0.80 (0.82)	0.79 (0.82)	0.86 (0.88)	0.85 (0.89)
NICS(0)	-9.63 (-8.53)	-8.83 (-7.73)	-8.79 (-7.83)	-9.72 (-8.45)	-9.64 (-8.49)
NICS(1)	-11.59 (-10.46)	-11.31 (-10.85)	-11.29 (-10.95)	-11.72 (-10.34)	-11.73 (-10.39)

Table 4. Descriptive parameters at the point critical point in the bond path between Cr and O4; electronic density $\rho(r)$, its Laplacian $\nabla^2\rho(r)$ and electronic energy density $E_d(r)$. Also the values of the atomic charges for the chromium and oxygen atoms are given.

parameter	3	4	5
$\rho(r)$ [e/a_o^3]	0.099	0.098	0.079
$\nabla^2\rho(r)$ [e/a_o^5]	-0.118	-0.128	-0.138
$E_d(r)$	-0.2110	-0.0063	-0.0036
Charge O	-1.154	-1.154	-1.148
Charge Cr	1.992	1.994	2.009

between Cr and O4 is negligible, if we compare atomic charges and the charge density at bcp for **3** and **4**. Interestingly, the changes in the Laplacian and electronic energy density are more clearly seen. The deprotonation at N1 results in changes that indicate weakening of the Cr-O4 bond. All of these results are in accordance with the experimental observation, that the compound 3 is stable in the solid state, but active in solution. This is especially seen in the electronic energy density values, which show clearly how the kinetic energy density contribution increases at bcp [20].

It is clearly seen in Fig. 5 that there is charge depletion in the bonds from chromium to oxygen. The bonds are polar, which is also seen in the relatively high atomic charges given in Table 4. Furthermore, the electronic energies for **4** and **5** have low values, which is indicative of a weak attractive interaction. This is further corroborated by the delocalization index, *e.g.* in **4** for Cr-O4 bond. The index value obtained by ELF is only 0.48, but for the other three Cr-O bonds the index is 1.76. The former value refers to a bond order that is less than one, and the latter one suggests a bond order less than two.

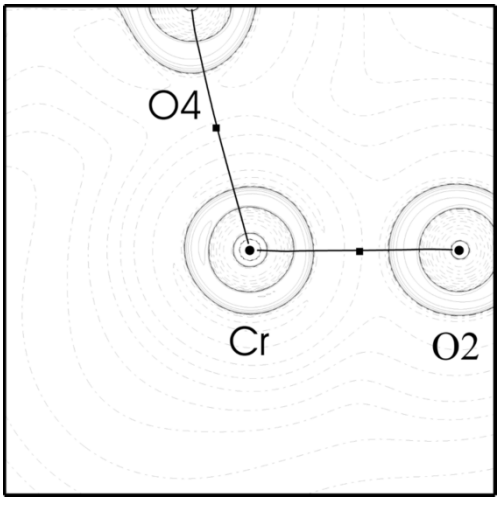


Figure 5. The negative Laplacian contour in the plane consisting of the central chromium atom and the oxygen atoms O2 and O4 for the compound $\mathbf{3}_{opt}$.

Supplementary Material

The atomic coordinates of the optimized structures and details of the X-ray structure determination.

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